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RULES FOR THE OCCURRENCE OF SUPERCONDUCTIVITY AMONG THE

ELEMENTS, ALLOYS, AND COMPOUNDS

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RULES FOR THE OCCURRENCE OF SUPERCONDUCTIVITY AMONG THE

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Gerhart K. Gaulé

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Abstract

    An empirical rule predicting the occurrence of superconductivity
among the elements was given by Matthias (Matthias Rule, MR). The MR
states that nonmetallic, ferromagnetic, and antiferromagnetic elements
do not become superconductors, and that the empirical laws applying to
the transition metals (TM) are quite different from those applying to
nontransition metals. Within these restrictions, the MR gives an
estimate of the expected superconducting transition temperature, T_c, in
terms of three parameters: (1) the atomic mass, M; (2) the atomic
volume V_a; and (3) the number of valence electrons per atom, n. The
crystal symmetry also has some influence on the T_c value. The MR for
the elements is with success applied also to alloys and compounds, when
proper averages over the M and n values of the constituent atoms are
used. Three supplementary rules pertaining to the influence of compound
formation on T_c are given by the author. The theoretical justification
for the established empirical rules is outlined. Certain characteristic
deviations from the MR are then discussed. A new rule is proposed for
systems which contain TM atoms in the form of "chains," or "prisms,"
such as the TM borides. In other systems not obeying the MR, unexpectedly
large changes of T_c are caused by small concentrations of vacancies, or of
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RULES FOR THE OCCURRENCE OF SUPERCONDUCTIVITY AMONG THE ELEMENTS, ALLOYS, AND COMPOUNDS

I.   INTRODUCTION

Since the discovery of superconductivity in mercury by Kammerlingh Onnes[1] in 1908, many other metals, alloys and compounds were found to be superconductors.   Contrary to expectations, however, no superconductors were found among the "good conductors," such as copper, silver, or gold. Another puzzling observation was the large variation of the superconducting transition temperatures, T_c, for the elements of the 4d and 5d transition series of the Periodic Table.   These "transition metals" are very similar in most of their properties and one would expect only a small variation in T_c.   The T_c values of many alloys and compounds seemed to pose a still greater riddle.   Unexpectedly high values were sometimes obtained by combining a superconducting element with a nonsuperconducting one, even a nonmetallic one, or by combining two nonsuperconductors.   Fortunately, the situation was greatly clarified by Matthias in 1957[2] when he established a set of simple empirical laws describing the occurrence of super- conductivity, as well as the variation of the T_c values within a given group of superconductors.   This set of empirical laws, usually called the "Matthias Rule," was first applied only to the elements, as discussed in Section II of this report.   The extension of the Matthias Rule into the field of alloys and compounds, which is particularly challenging because of the wealth of experimental information available, is treated in Section III.   Section IV presents the theoretical justification, first established in 1958 by Pines,[3] for the basically empirical Matthias Rule. Section V discusses the superconducting properties of the transition metal-borides, a family of materials which disobeys the Matthias Rule.[4]

Other deviations from the rule, some of which were discovered only very recently, are treated in Section VI. A summary of the results and the conclusions drawn are presented in Section VII and Table II.

II. THE MATTHIAS RULE FOR THE ELEMENTS

The Periodic Table of the Elements according to Kessler[5] gives an excellent synopsis of the electronic properties of the elements. In Figure 1, the table has been adapted for this work by adding the T_c values of elements, and of certain compounds. The electronic properties are discussed first. Each atom differs from its predecessor in the sequence of atomic numbers (which are marked to the left of the element symbols) by one electron. The vertical position of the element symbol indicates the atomic subshell (marked on the left of the table), to which this "last" electron was added. Sometimes another electron is simultaneously added to the subshell. This is then always at the expense of another subshell, as indicated by appropriate symbols in Figure 1. The Periodic Table so obtained gives an instructive and "natural" presentation of the d-transition series (transition metals), as well as the f-transition series (rare earths and actinides). Similarly, the groupings of the non-transition metals, and the nonmetals, are easily recognized in the left and the right portions of the table. A grouping with respect to the superconducting transition temperatures, T_c, of the elements is also given in Figure 1. The approximate T_c value for each superconducting element is listed over the atomic number. Most of these values were obtained from the excellent compilation by Roberts.[6] For the graphical representation of the superconducting properties, the temperature scale has been divided into ranges, using powers of 2 for the limits, as indicated in Figure 1. A symbol denoting the temperature range which

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contains T_c is placed to the immediate right of the atomic number of each superconducting element. For convenience, a coarser classification is also used in this work. Superconductors with a (relatively) high transition temperature $T_c \geq 8°K$ are called "high temperature superconductors," and those with $T_c < 2°K$ "low temperature superconductors," the rest "medium temperature superconductors."

The T_c data of Figure 1 are now discussed in terms of the empirical laws found by Matthias,[2] which are formulated here as follows:

(1) No superconductivity is found among elements which are:

    (a) nonmetals, semiconductors, or semimetals

    (b) ferromagnetic or antiferromagnetic

(2) With n for the number of valence electrons, superconductivity is found only in elements for which $2 \leq n \leq 8$.

(3) The variation of T_c with n is given by an empirical function $T(n)$, qualitatively shown in Figure 2. For a given d-transition series, $T(n)$ has relative maxima at n = 3, 5, and 7, and relative minima at n = 4, and 6. For a sequence of nontransition metals, $T(n)$ increases monotonically with n.

(4) With V_a for the atomic volume, and M for the atomic mass, T_c varies for a given n as follows:

$$T_c \propto V_a^u / M^w$$

with $\qquad\qquad 4 < u < 5.$

Observed T_c differences between isotopes of a number of elements[7] suggest: $w = \frac{1}{2}$. Elements at the limits given by (2), i.e., with n = 2 and n = 8, show no regular variation of T_c with V_a and M.

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(5) The crystal structure has some influence on T_c. Uncomplicated

cubic and hexagonal systems appear "favorable" to super-

conductivity. The variations in T_c which can be attributed

to differences between structures are generally small (20% to

30%).

With the help of the empirical laws (1) and (5), the Matthias Rule
can be represented by a single equation:

$$T_c = [C \, V_a^u/M^w] \, T(n) \qquad (II.1)$$

$$u \approx 5, \ w \approx \tfrac{1}{2}.$$

The expression in the square bracket is dimensionless and of the order

one. C varies with crystal structure as discussed in (5) above. C

and $T(n)$ may be so adjusted that the expression in square brackets in

(II.1) becomes unity for niobium and that $T(5) \approx 9°K$, the T_c value of

Nb. The T_c values of the horizontal, vertical and diagonal neighbors

of this "pivotal" superconductor are then easily predicted by (II.1).

Comparison with the actual values of Figure 1 shows good agreement. The

formula (II.1) indicates, for example, why Nb is a superconductor superior

to both its vertical neighbors. Vanadium, although having an atomic mass,

M, smaller than that of Nb, also has a substantially smaller atomic volume

V_a, and the latter influence prevails. The reverse is true for the

relation between Nb and Ta.

Figure 1 shows Nb and Tc as the only high temperature superconductors

(in terms of the definition given above) among the elements. Their common

horizontal neighbor, Mo, however, rates as a low temperature super-

conductor. This is, of course, just the verification of two of the

"peaks" and of one "valley" stipulated by the $T(n)$ curve in Figure 2.

Further verification is obtained by inspecting the 4d and 5d transition

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series in Figure 1. The 3d transition series yields little information, because the "peak" ($n = 5$) superconductor V is followed by antiferromagnetic and ferromagnetic elements. In agreement with the rule (1), above, these elements are marked with a "0," indicating that no superconductivity is expected. Se, Y, and some other elements are marked with a "?," indicating that superconductivity may be found in the future when measurements on samples of higher purity, or measurements at lower temperatures, are made. Thus, superconductivity is suggested for Sc and Y by the Matthias Rule, and by analogy to the superconductor La in the same column. Super-conductivity was also predicted for Lu,[8] which differs from La only insofar as La has a completely empty 4 f shell, and Lu a completely filled 4 f shell. Elements with partly filled 4 f shells ("rare earths") have dominant magnetic properties and do not superconduct. In contrast to this, at least one element with a partly filled 5 f shell, U, is a superconductor.

Inspection of the nontransition metals of the Periodic Table, Figure 1, reveals only fair agreement with the Matthias Rule. Of some interest is the sequence Hg, Tl, Pb, Bi. The value for Hg is "too high" for a divalent element. Bi is a semimetal and, of course, a nonsuperconductor. A high-pressure phase of Bi, and also an amorphous phase of Bi obtained by low temperature condensation,[9,10] are high temperature superconductors. It is assumed that Bi loses its semimetallic character upon formation of one of these two phases, and becomes metallic. The observed T_c values are indeed slightly higher than those of Pb, as predicted by the Matthias Rule for a metallic right neighbor of Pb (Figure 2). The amorphous phases of Be and Ga, which are also high temperature superconductors, represent obvious deviations from the Matthias Rule.

III. RULES FOR ALLOYS AND COMPOUNDS

Some slight modifications of the Matthias Rule for the elements produce an equivalent rule for compounds and alloys.[2] These modifications are conveniently formulated in close analogy to the empirical laws (1) through (5) of the previous section (see also Table II):

(1'a) Materials with the electronic properties of nonmetals, semi-conductors, or semimetals do not superconduct.

(1'b) Antiferromagnetic materials do not become superconducting.

(1'c) Ferromagnetism resulting from d-spins, i.e., from unpaired electrons in partly filled d-subshells, is not compatible with superconductivity.

(1'd) Ferromagnetism resulting from f-spins is in special cases compatible with superconductivity.

The last statement reflects observations made by Matthias[35] on pseudobinary systems such as YOs_2 with a few percent $GdOs_2$ in solid solution. By proper adjustment of the Gd content, a material is obtained which first becomes ferromagnetic and then superconducting upon cooling.

(2') With n now denoting the average number of valence electrons per atom of the alloy or compound, the occurrence of super-conductivity is again limited by:

$$2 \leq n \leq 8.$$

(3') The variation of T_c with n is again given by an empirical function $T(n)$, which resembles that for the elements (Figure 2), but with the second maximum shifted to n = 4.7 and the third maximum shifted to n = 6.7.

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(4') With V_a now denoting the mol-volume, the variation of T_c for

a given n may be expressed by:

$$T_c \propto V_a^u \cdot f(M_1, M_2); \quad 5 < u < 10.$$

No simple function $f(M_1, M_2)$ describing the combined influence

of two atomic masses M_1, M_2 can be given although it is evident

that large masses tend to decrease T_c.

(5') The uncomplicated cubic and hexagonal systems which had been

recognized as "favorable" to high T_c values for the elements

are of equal importance for alloys and compounds. Several

superconductors in the highest T_c range are intermetallic

compounds of the type TM_3L (with "TM" for "transition metal,"

and "L" for another element) and crystallize in the so-called

β-W structure,* which has no analogue among the elements.

Numerous complicated structures are found among the medium

and low temperature superconductors. No superconductors

have been found having crystal structures without a center

of inversion.

Of special interest is the occurrence of superconductors with high

T_c values. To study this problem, the T_c value of a selected super-

conducting compound (if existing) is presented over each element symbol .

in Figure 1. The formula of the compound is placed to the immediate left

of the T_c value. The compound (or alloy) selected is the one with the

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*The "β-W" structure does not occur in elemental W, as originally
assumed, but only in W_3O. See[12].

highest T_c value among all the binary compounds (or alloys) with at least 50 atomic percent of the element considered. Most of these T_c values are again taken from the compilation by Roberts.[6] The data for selected compounds in the Periodic Table, Figure 1, suggest the establishment of three additional empirical laws, which may be considered as complementary to the Matthias Rule. The following statements pertain only to compositions with at least 50 atomic percent of the element in question:

(A) The T_c values of all superconducting elements are substantially raised upon formation of suitable compounds or alloys. The increases are 50% and more for transition metals, and generally less for nontransition metals.

(B) With the exception of the elements of the f-transition series, and of the 7a and the 0 columns of the Periodic Table, most nonsuperconducting elements form superconducting alloys or compounds.

(C) Elements which become superconductors, or superconductors which attain increased T_c values upon formation of an amorphous phase, behave similarly upon formation of a suitable compound.

The vast experimental material available on superconducting alloys and compounds generally supports the simple rules formulated in this section. Structural aspects are extensively treated in the work of Matthias.[2,11] Superconducting solid solutions with a wide homogeneity range permit the continuous variation of the electron concentration, n. Chanin, Lynton and Serin[13] dissolved In or Sb in Sn and showed that the observed variation of T_c with n is that predicted by the Matthias Rule, except for small concentrations. The consequences of these results are also discussed by Coles.[14] Extensive studies of solid solutions formed

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by transition metals reported by Hulm and Blaugher[15] confirmed the two predicted T_c maxima at n = 4.7 and n = 6.4. No clear relationship could be established, however, for alloys formed between vertical neighbors in the Periodic Table.

The Matthias Rule for transition metals is generally obeyed also by compounds formed between transition metals and nontransition metals. This has been demonstrated by Matthias[2] by comparing many compounds of Mo, W, Nb or V with nontransition metals. Even compounds with the semiconductors Si and Ge do not deviate from the T(n) curve for transition metal compounds. To determine whether the Matthias Rule for transition metals would still apply to compounds between transition metals and such pronounced nonmetals as B, C, and N, a comparison of these compounds was made by the author.[4] Since the 3d-transition series contains only two superconductors, the comparison was limited to the borides, carbides and nitrides of the 4d- and 5d-transition metals. The results are presented in Figure 3 by plotting the highest reported[6] T_c values for all three kinds of compounds as a function of n. The maximum T_c values obtainable from binary combinations of 4d- and 5d-transition metals alone are also shown. This "reference" curve shows the characteristic peaks at n = 4.7 and n = 6.7. The two curves representing the carbides and the nitrides both have a very pronounced peak near n = 5, and "dips" near n = 4 and n = 6. The boride curve, having a peak at n = 4, and a dip at n = 4.5, is clearly "out of step" with the three others. With these somewhat surprising results, the borides appear to be the only family of transition metal-nonmetal compounds which clearly violates the Matthias Rule. The transition metal borides are discussed in more detail in Section V.

IV. THE THEORETICAL BASIS FOR THE MATTHIAS RULE

An approximate relationship between the properties of a superconducting material and its superconducting transition temperature, T_c, is given by the Bardeen-Cooper-Schrieffer ("BCS") theory.[16,17] The superconducting state is explained in this theory as the result of a many-body interaction among the electrons near the Fermi surface via the exchange of phonons. With respect to T_c, the theory predicts that:

$$kT_c = k\theta . e^{-1/N(0)V} \approx \hbar\omega . e^{-1/N(0)V} \qquad (IV.1)$$

where k is the Boltzmann constant, θ the Debye temperature, $\hbar\omega$ the average phonon energy, and $N(0)$ the number of electrons per unit energy near the Fermi surface, divided by the volume of the sample. -V gives the average net interaction energy between the electrons near the Fermi surface, multiplied by the volume of the sample. In the superconducting state, this net interaction energy is negative (attractive case), so that V is always positive when (IV.1) applies. Pines pointed out in 1958[3] that the then new BCS theory should explain many of the empirical features of the Matthias Rule. For the treatment of the nontransition metals, Pines neglects the influence of the lattice periodicity and assumes a gas of interacting electrons. In the gas, the Coulomb interaction between two electrons is reduced by the "screening effect" of the mobile charges of the other electrons. The amount of reduction is given by a screening parameter, k_s. This important parameter is related to the quantities V_a (atomic volume), and n (number of valence electrons per atom) from the Matthias Rule as follows:

$$k_s \propto (r)^{1/2}; \quad r = (3V_a/4\pi n)^{1/3}. \qquad (IV.2)$$

The new quantity, r, which is introduced for convenience, denotes the "electron spacing." It is related to V_a/n, the inverse electron density, as indicated. The phonon interaction between two electrons involves Coulomb interactions with ions, which are also "screened" with the same screening parameter, k_s. The rather complicated expression which Pines derives for the interaction energy, -V, contains an "attractive" phonon term and a "repulsive" Coulomb term. The phonon term is proportional to the square of the ionic charge, $(en)^2$. Therefore, the phonon term increases rapidly with n, giving superconductivity for $n \geq 2$ in accordance with the Matthias Rule. An increase in the screening parameter, k_s, also enhances superconductivity, since it reduces the Coulomb term more than the phonon term. According to (IV.2), k_s increases with the atomic volume, V_a. Thus, a large V_a enhances superconductivity again in accordance with the Matthias Rule. It is also seen in (IV.2) that a large n reduces k_s. This counteracts to some degree the influence of n via the ionic charge. Observing that $N(0)$ $\propto 1/r$ in his simple model, Pines[3] then expresses the exponent in (IV.1), $-N(0)V$, as a function of n and r, or in view of (IV.2), of n and V_a. The expression is not dependent on the atomic mass, M; the relevant terms cancel out in Pines' calculations of V. The mass dependence of T_c is contained in the first factor of (IV.1), the Debye temperature, θ, which varies as $\theta \propto M^{-1/2}$. With this, T_c is now connected to the three parameters of the Matthias Rule, M, n, and V_a through the BCS formula, (IV.1). In the treatment of Pines, the formula gives roughly the same trends for the T_c values of nontransition metals upon variation of any of the three parameters as the Matthias Rule. But the $N(0)$

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values actually calculated by Pines[3] are much too small to yield the correct range of T_c values. Pines notes that the simple, "free electron gas" relationship $N(0) \propto 1/r$ leads to discrepancies for metals with n = 2. As discussed above in Section II, (4), the Matthias Rule equally fails to make clear predictions for these elements. Pines points out that the divalent elements have basically one valence band filled with the two s-electrons, and that the metallic properties are only the result of a certain degree of band overlap. Therefore, the model of a gas of nearly free electrons is quite inappropriate. The model is, of course, even more inappropriate for the transition metals with their narrow and complex d-bands, making a different approach necessary.

Horizontal neighbors within a transition series are generally more similar to one another than horizontal neighbors in the Periodic Table among the nontransition metals. In particular, there is relatively little change in the room temperature resistivity within a given transition series. Since the high temperature resistivity depends on the phonon-electron interaction, this indicates a nearly constant interaction term, V, in the BCS formula (IV.1). Recent direct determination of V by Bucher et al.[18] shows a linear increase of V with n which is neglected for the following qualitative arguments. The large variations of T_c with n within a given transition series have been discussed in the preceding sections. In view of the BCS formula (IV.1), these large variations must be attributed to equivalent variations of $N(0)$, since θ and V are nearly constant within a given series. The variations of $N(0)$ with n can be predicted from theoretical computations of the electron level density, $dn(\epsilon)/d\epsilon$, for all the conduction bands of a given metal.

The characteristic features of the conduction band in metals, as far as known, are treated in detail by Slater.[19] The results of Manning and Chodorov,[20] also discussed by Seitz,[21] for the 5d transition series are presented in Figure 4. The upper curves represent the level densities for the individual bands (I through V for the d-bands, VI for the s-band) as functions of the energy; the lower curve gives the total densities of all six bands combined. Integration over $dn(\epsilon)/d\epsilon$ from zero energy (the "bottom" of the lowest band) to the Fermi energy yields the total number of electrons per atom, n. The BCS quantity, $N(0)$, is proportional to the value of $dn(\epsilon)/d\epsilon$ at the Fermi energy. The Fermi energies for Ta (n = 5), and W (n = 6) are indicated in Figure 4. A characteristic dip is recognized near n = 6, as predicted by the Matthias Rule. The effect of the dip is greatly magnified through the exponential character of the BCS formula, (IV.1). Setting, for convenience:

$$N(0)V = G$$

one easily verifies that

$$\Delta T_c/T_c = (1/G)\Delta G/G. \qquad (IV.2)$$

G is usually between 0.3 and 0.2 for medium temperature superconductors. Formula (IV.2) then states that a 10% change in G, or $N(0)$, is reflected by a 30% to 50% change in T_c, and so forth. The large volume exponent, u, in the expression $T_c \propto V_a^u$ of the Matthias Rule becomes plausible by similar reasoning. The magnifying effect of (IV.2) is obviously reduced for large G values (G ≈ 0.4). This could possibly explain why the T_c vs. n curves for transition metals, for example those of Hulm and Blaugher,[15] often have flat "peaks," but steep "valleys." For the hypothetical case of G >> 1, T_c would evidently approximate the Debye temperature, θ.

Experimental $N(0)$ curves are available from measurements of the specific heat, γ, which is proportional to $N(0)$. Daunt recognized in 1955[22] the similarity between the T_c variations and the γ variations within a transition series. Recent experimental data by Hoare[23] are presented in Figure 5. It is seen that the actual variations of $N(0)$ are considerably greater than the calculated ones of Figure 4. The agreement with Matthias Rule is excellent except for $n > 8$, where the γ vs. n curves predict high temperature superconductivity for nonsuperconductors such as Pd and Pt. The data on Figure 4 also demonstrate some of the influence of structure. It can be seen, for example, that the γ increase from W to Pd is not as large as expected, probably due to the change in structure.

Morel and Anderson[24] recently presented a theory which leads to rather accurate predictions for the $N(0)V$ values of transition metals as well as nontransition metals. The phonon term used by these authors is based on a retarded interaction via short wavelength phonons. This is in contrast to the "umklapp"-processes, which were considered of primary interest by Pines.[3] Another improvement is the use of experimental data, instead of free electron data, for $N(0)$. A somewhat strange result of the theory of Morel and Anderson is the prediction of superconductivity for all (non-ferromagnetic) metals. The calculation yields a positive (attractive) $N(0)V$ value even for the monovalent metals Na, K, Cu, Au. The predicted $N(0)V$ values are very small, however, so that these materials would become superconducting only at temperatures of the order 10^{-3}°K or less. An experimental test of this prediction would be extremely difficult.

In the discussion of repulsive and attractive interactions in this section, no distinction has been made so far between s- and d-electrons. Such a distinction is suggested by the considerably heavier effective masses of the d-electrons. Garland[25] and Peretti[26] have recently shown that a superconducting state can exist by virtue of s-d interactions. These interactions do not necessarily involve phonons. In that case, the BCS formula, (IV.1), would not have the Debye temperature, θ, as a factor (and as an upper limit for T_c). Since θ is, by virtue of $\theta \propto M^{-1/2}$, responsible for the isotope effect (see Section II) a "phonon independent" superconductor should have no isotope effect. It is indeed known that Ru and Os have no isotope effect, and that some other superconducting materials show only a partial isotope effect.[27] This gives support to the idea of an s-d interaction not involving phonons. For the case of predominant s-d interaction, Peretti replaces the expression $N(0)V$ in the BCS formula (IV.1) by: $[N_s(0)N_d(0)]^{1/2}V_{sd}$. The indices are self-explanatory. An estimate of the magnitudes of the two density terms $N_s(0)$ and $N_d(0)$ and of their variation with n may be made with the help of Figure 4.

The absence of superconductivity among nonmetals, semiconductors, and semimetals is quite obvious from the preceding discussion; these materials do not have a sufficient number of conduction electrons; the $N(0)$ values are too small. The BCS model serves to explain why d-spin ferromagnetism is not compatible with superconductivity. The model imposes rigorous restrictions on the spins of the electrons near the Fermi surface (which are mainly from the d-bands) in assembling these electrons in "Cooper pairs"[16,17] with zero net momentum and zero net spin. The

electrons cannot simultaneously fulfill the equally rigorous and quite different requirements imposed by ferromagnetic spin alignment. Similar reasoning applies to d-band antiferromagnetism. The situation may be different in the case of f-band ferromagnetism (Section III, (1'd)), because f-electrons are localized. No satisfactory theoretical explanation for the absence of superconductors among the nonferromagnetic transition metals with $n > 8$ has been given.

V.   THE MODIFIED MATTHIAS RULE FOR THE TRANSITION-METAL BORIDES

A survey of the T_c vs. n curves of the three most important families of superconducting transition metal-nonmetal compounds, namely, the transition-metal borides, -carbides and -nitrides was presented in Figure 3 and discussed at the end of Section III. It was shown that the curve for the borides is "out of step" with those for the two other families, and of course also at variance with the Matthias Rule. This motivated the author and his co-workers[4] to prepare borides with possibly high transition temperatures and with an average number of valence electrons, n, within the range of the observed discrepancy, $4 \leq n \leq 5$. The preparation of satisfactory boride samples is difficult because of the very-high melting points and of the often complicated phase diagrams. These problems are extensively discussed by Schwarzkopf and Kieffer.[28] Reactive sintering (S) and direct fusion (M) permit synthesis at a temperature lower than the melting temperature, which is often required by the phase diagram and by other considerations. The letter symbols, S and M, serve for a convenient identification of materials in the following. Many samples prepared by sintering or fusion were subsequently melted in a vacuum by an electron beam (E). The electron beam melting was often combined with floating zone

refining. Electron beam melted and, even more so, zone refined samples are generally superior to others in purity and structural perfection. This may be seen from Table I, which gives a detailed comparison of typical S, M, and E samples.

The results obtained with borides from the three methods of preparation used are summarized in Figure 6. For comparison, the top curve gives the highest values from the literature,[6] the same as in Figure 3. The observed T_c ranges for samples of a given origin are indicated by brackets. In the case of NbB (n = 4), the trends are as expected. The sintered material has a wide spread of T_c values, and is inferior to the electron beam melted material. The electron beam material does not quite reach the value expected from the literature, probably due to loss of B by evaporation at the very-high melting temperature of NbB ($\approx 2800°C$). It is possible that the so induced boron vacancies in the NbB lattice depress the T_c value of the material, as discussed in the next section. In spite of these small differences, the new T_c values for well-prepared NbB material evidently confirm the "wrong" peak at n = 4. The situation with MoB (n = 4.5) is similar. None of the samples, which had been prepared in various ways (see Table I), were found superconducting above 1.6°K, the limit of the measuring apparatus. Thus, the "dip" at n = 4.5 is also confirmed by the new measurements.

The results for Mo_2B (n = 5) appeared rather paradoxical. The T_c data for fused and for sintered material have only small spreads and agree well with the published data. Upon electron beam melting, however, the values become unexpectedly low. In view of the high T_c values for the Mo-nitrides (12°K for MoN, 5°K for Mo_2N) and the vigorous outgassing

observed during the electron beam melting process, the influence of nitrogen, possibly in solid solution in the Mo_2B system, was suspected. To test this idea, an outgassed, low T_c sample was heated in a nitrogen atmosphere. This treatment raised the T_c value back into the range for material which had not been outgassed. These results strongly suggest that the T_c values of the electron beam melted material are more representative for Mo_2B in its purest form. The new T_c vs. n curve in Figure 6 is drawn accordingly. It is seen that a "valley" now extends from n = 4.5 to n = 5, creating an even greater deviation from the Matthias Rule.

An explanation for the unusual T_c vs. n curve for the transition metal borides is suggested by the unusual electronic and structural properties of elemental boron[29] as well as many transition metal-borides.[28,30] In contrast to the uncomplicated NaCl or other cubic, or hexagonal structures of most of the carbides or nitrides, the metal rich borides are usually characterized by two interleaved substructures, one containing only transition metal (TM) atoms, the other only B atoms. Figure 7 shows that the monoborides NbB, β-MoB, TaB, and CrB, arrange the TM atoms in endless trigonal prisms, with the B atoms forming zigzag chains in channels between the prisms;[28] δ-MoB has a similar structure. The subborides γ-Mo_2B and Ta_2B, shown in Figure 8, have linear chains of B atoms. Each B-chain is located at the center of four parallel chains formed by the TM atoms.[28] The TM chains are built by distorted tetrahedra sharing edges. It appears very plausible that TM-TM and B-B bonds are much more numerous in such a system than the "mixed" TM-B bonds.[30] In that case, little "sharing" of electrons between the two subsystems and little change in the nature and occupation of the d-band of the transition metal would occur upon formation

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of such a compound. The normal and superconducting properties of mono-borides and subborides should approximate those of the metal. To test this assumption, the number of the electrons per atom of each metal, n^*, is also given in Figure 6. In terms of n^*, the TM-borides have indeed "regular" behavior, with a peak at $n^* = 5$, and a valley at $n^* = 6$.

Valuable information on the electronic properties of a superconductor can be obtained by measuring the normal conductivity under various conditions. One obvious criterion for the metallic character of a material is the resistivity at room temperature, ρ_{300}. The data in Table I indicate that the ρ_{300} values for an electron beam melted transition metal boride sample are low, in the neighborhood of the ρ_{300} value of the transition metal itself. Another important criterion is the variation of ρ, the resistivity, with temperature. Plots of ρ/ρ_{300} for typical samples are presented in Figure 9. The curves for sintered and fused samples tend to level off below 50°K, indicating a temperature behavior of ρ which is the result of strong scattering by impurities or structural imperfection.[19] The curves for the electron beam melted samples drop to much lower values before superconductivity is reached. These results and those from the structural and the chemical analysis presented in Table I seem to justify the assumption made above, namely that the electron beam melted samples of Mo_2B, in spite of their low T_c values, are more representative than the other samples for the "ideal" properties of Mo_2B.

VI. OTHER DEVIATIONS FROM THE MATTHIAS RULE

The Matthias Rule predicts only mild variations of the T_c values upon the introduction of a few percent of impurities into the metal. That this is so even for the transition metals can be understood in terms of the

structure of the s-bands and d-bands discussed in Section IV and schematically presented in Figure 4. Although according to this picture, a small shift in the Fermi energy may cause dramatic changes of the electronic properties, many additional electrons (a fraction of one electron per atom) are necessary to change the filling of the bands, and thus the Fermi energy, significantly. This is in contrast to the situation in semiconductors. These also depend very strongly on the position of the Fermi energy with respect to the conduction band, but a large shift of the Fermi energy can be accomplished with a few additional electrons ("doping" with foreign atoms more electro-negative than the host atoms).[21]

Changes in T_c much larger than expected from the calculated change of n in the general empirical $T(n)$ function of Section II are therefore considered exceptions to the Matthias Rule. Such an exception was recently observed by Giorgi et al.[31] in TaC and NbC. Although these materials have a wide homogeneity range, a small deficiency of carbon in these high temperature superconductors causes a sharp drop in T_c, much sharper than expected from the Matthias Rule. Boron deficiency in the high temperature superconductor NbB may have a similar effect, as discussed in the previous section. The very large decrease in T_c resulting from the "outgassing" of Mo_2B, and the reversed effect, also discussed in the previous section, fall into the same category. The observed loss of nitrogen during the outgassing is very small ($\approx$ 0.02% of the sample as indicated in Table I), but it may possibly induce a considerable change in the concentration of boron vacancies or the like. An analogue to the outgassing effect in Mo_2B was reported by Picklesimer and Sekula[32] for technetium. These authors reduced the T_c value of technetium from 11.2°K to 8.22°K through purification, essentially the removal of small amounts of oxygen.

Reed et al.[33] recently discussed systems in which the influence of the average number of electrons per atom, n, is smaller than expected from the Matthias Rule and also small in comparison to the influence of structural order. One system studied was of the kind Nb_3Sn (n = 4.75), with considerable Nb surplus, with the highest surplus represented by Nb_4Sn (n = 4.8). In spite of the large Nb surplus, the β-W structure (see Section III) was preserved in the material either by replacing Sn with Nb atoms or possibly by creating an appropriate number of Sn vacancies. The T_c value increased only slightly by going from Nb_3Sn to Nb_4Sn. A largely decreased T_c value is observed, however, in samples with atomic disorder, that is, with Sn atoms on Nb sites. Reed et al.[33] point out that the Nb atoms form perpendicular chains in the β-W structure. The Nb-Nb distance in the chains is 10% shorter than in elemental Nb. The authors speculate that the Nb chains are responsible for the high temperature superconductivity of Nb_3Sn, making T_c very sensitive against "disruption" of Nb chains by disorder. An enhancement of superconductivity by structural disorder was found by Matthias[2] in superconductors such as PdTe which crystallize in the NiAs structures.

When small concentrations of atoms of a ferromagnetic element are introduced into a superconducting material, the result is usually a reduction of the T_c value sharper than that predicted by the Matthias Rule. A good example is Fe in Mo.[34] Introduction of about 0.02% Fe into pure Mo depresses the transition temperature from 1°K to 0.1°K. There are numerous cases, however, where the introduction of ferromagnetic impurities causes an unexpectedly large enhancement of superconductivity. These cases

were surveyed by Matthias in 1960.[35] No clarification of the effects
caused by small amounts of ferromagnetic elements in superconducting
materials can be expected before a satisfactory theory for the s-d inter-
actions becomes available.

VII. SUMMARY

   The Matthias Rule still serves as an excellent tool to predict the
occurrence of superconductors and to predict their transition temperatures,
although significant deviations from the rule have been discovered since
its inception in 1957. In the present work, the Matthias Rule is formulated
in the convenient form of a set of five empirical laws. Three new empirical
laws pertaining to the occurrence of high temperature superconductivity
among alloys and compounds have been added (Section III; for a survey of all
the discussed rules, see also Table II). No serious discrepancies between
the formulated empirical laws and the most recent theory have been found
except for some of the transition metals with more than eight valence
electrons, for which the theory wrongly predicts high temperature super-
conductivity (Section IV). A notable exception from the Matthias Rule is
given by the family of superconducting transition metal borides. The
peculiar arrangement of the boron and of the transition metal atoms in
endless chains or endless prisms was determined as the cause of this
exception and the Matthias Rule was accordingly modified for the transition
metal borides (Section V). Other compound systems containing transition
metal atoms in the form of chains show related deviations from the Matthias
Rule. More difficult to understand are systems in which unexpectedly large
changes of the superconducting properties are caused by small concentrations
of structural vacancies, or of impurity atoms such as nitrogen or oxygen, or

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of impurity atoms from ferromagnetic elements such as iron (Section VI). The exceptions to the Matthias Rule present a serious challenge to solid-state physics. A more adequate model of the s-d interactions is expected from the theory, covering magnetic effects as well as superconductivity. More extensive studies of the systems with known deviations from the Matthias Rule and a vigorous search for new systems of this kind are also needed. Experimental work of this kind should yield more comprehensive and more accurate empirical rules for the occurrence of superconductors, among the alloys and compounds. This, together with a clearer theoretical insight into the various and conflicting influences on the transition temperatures within a given family of materials, would eventually produce highly reliable guidelines for the development of new superconducting materials.

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Periodic Table with the Transition Temperatures of the Superconducting Elements
and of Selected Compounds

Figure 1

Periodic Table: Elements are placed according to the subsequent introduction of electrons into the

atomic subshells, marked on the left, following Kessler.[5] ▲ indicates gain of an additional

electron from another subshell, with ↑ denoting the losing subshell (example: Ca, Cr).

Note: Gd should be in the same block with Pt, but was raised one block for clarity.

Superconducting Transition Temperatures (T_c, in °K): T_c for element over atomic number, T_c for

selected compound over element symbol. Formula of selected compound in between (example:

Nb + ¼ Sn → Nb$_4$Sn). Among the compounds (or alloys) containing at least 50 atom percent of the

element considered, the one with the highest T_c is selected.

Crystal Structures: Symbols bcc (body centered cubic), hcp (hexagonal close packed), fcc (face centered

cubic), pertain to 4d transition series only.

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SUPERCONDUCTIVITY OF THE ELEMENTS
AND OF
SELECTED ALLOYS & COMPOUNDS

Figure 1

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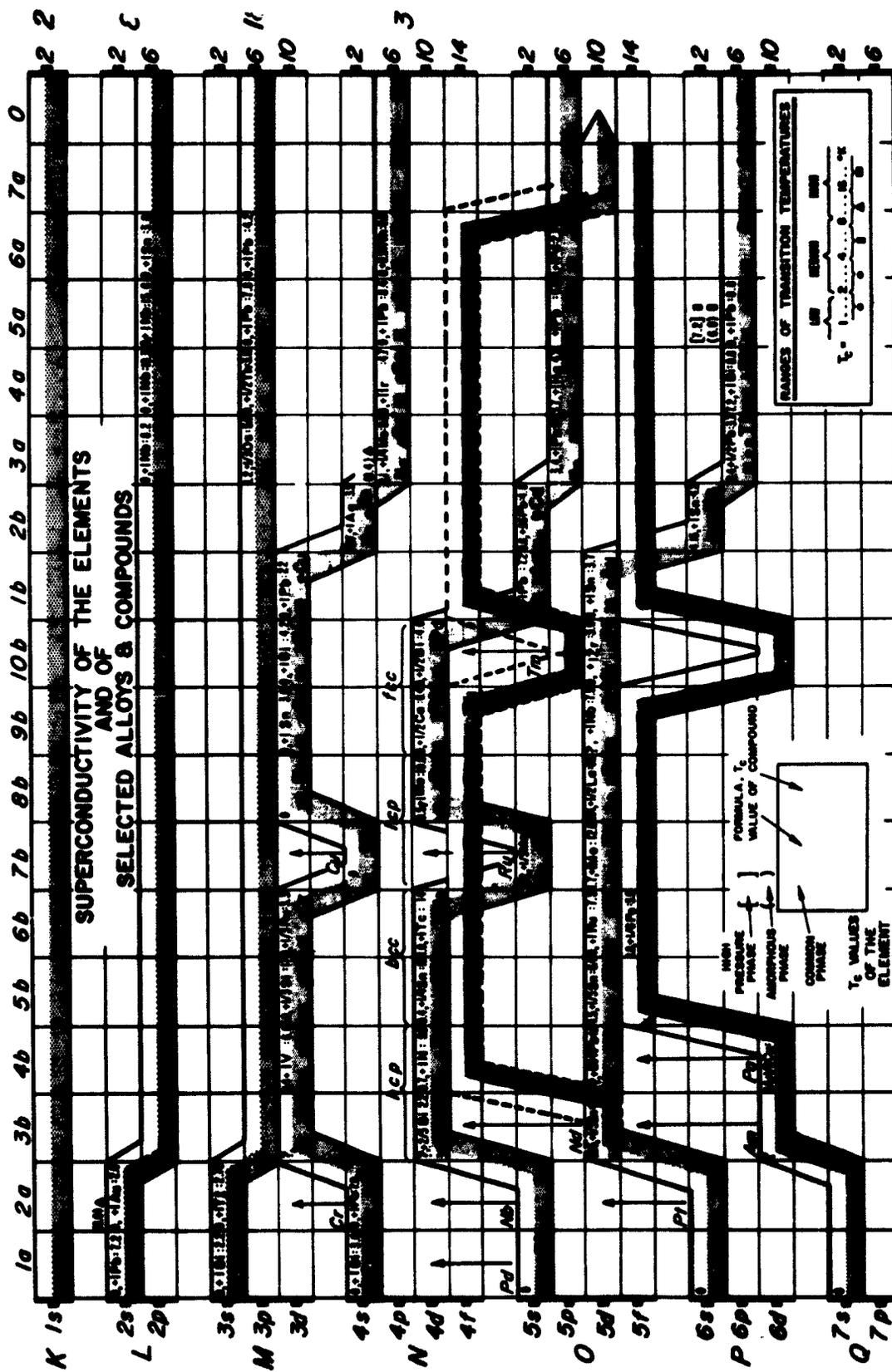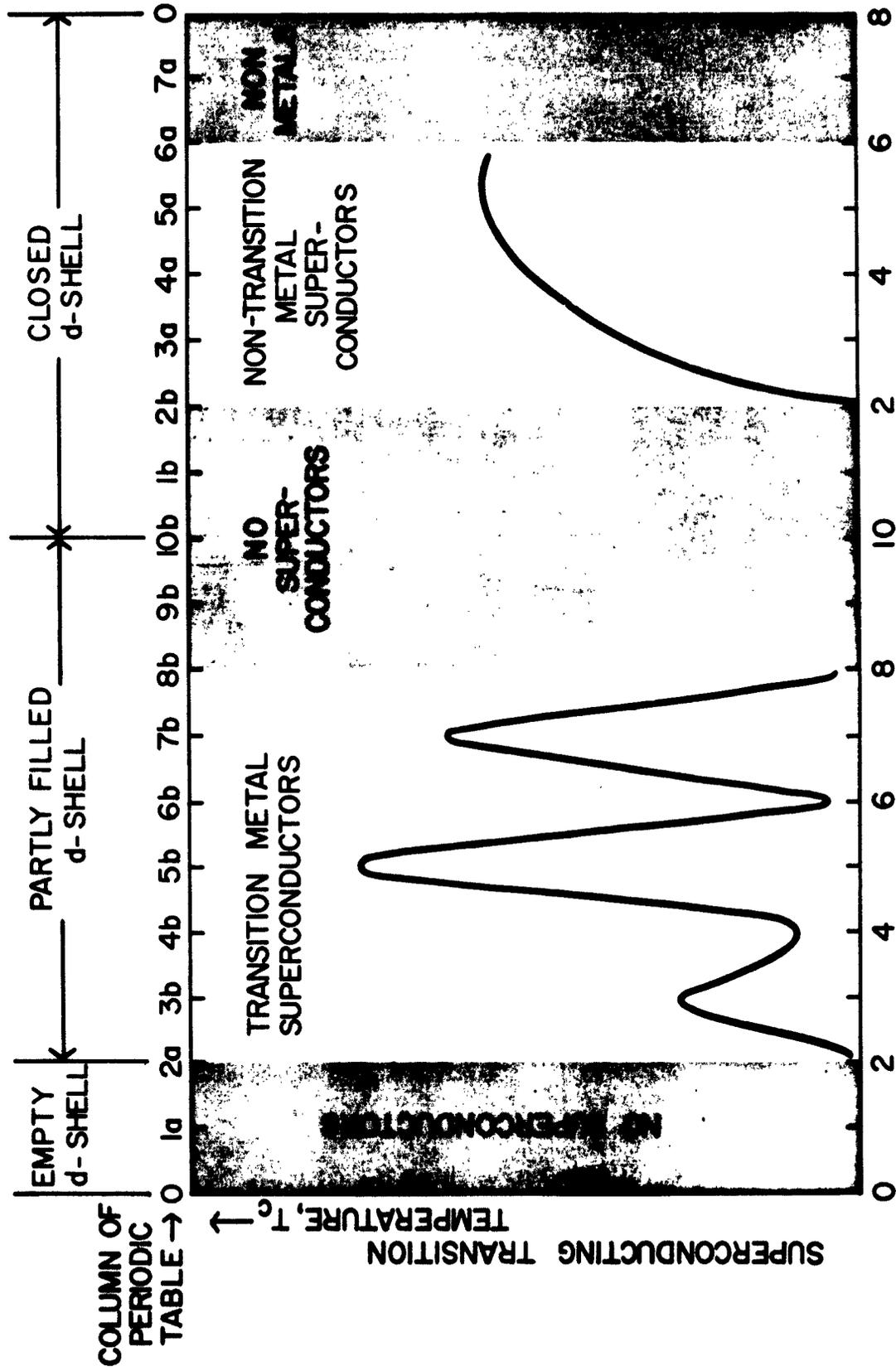
Figure 2   Characteristic T_c vs. n curve for a horizontal row of the Periodic Table not containing ferromagnetic elements (after Matthias[2]).

TRANSITION METALS (TM) CONSIDERED								
n	3	4	5	6	7	8	9	10
4d	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
5d	(La)	Hf	Ta	W	Re	Os	Ir	Pt

| TM-SERIES	TM ALLOY OR ELEMENT	TM-CARBIDES	TM-NITRIDES	MONO-BORIDES TMB	SUB-BORIDES TM_2B
4d	●	■	▶	◉	▣
5d	●	■	▶	◉	▣
4d+5d	●	■	▶	◉	▣
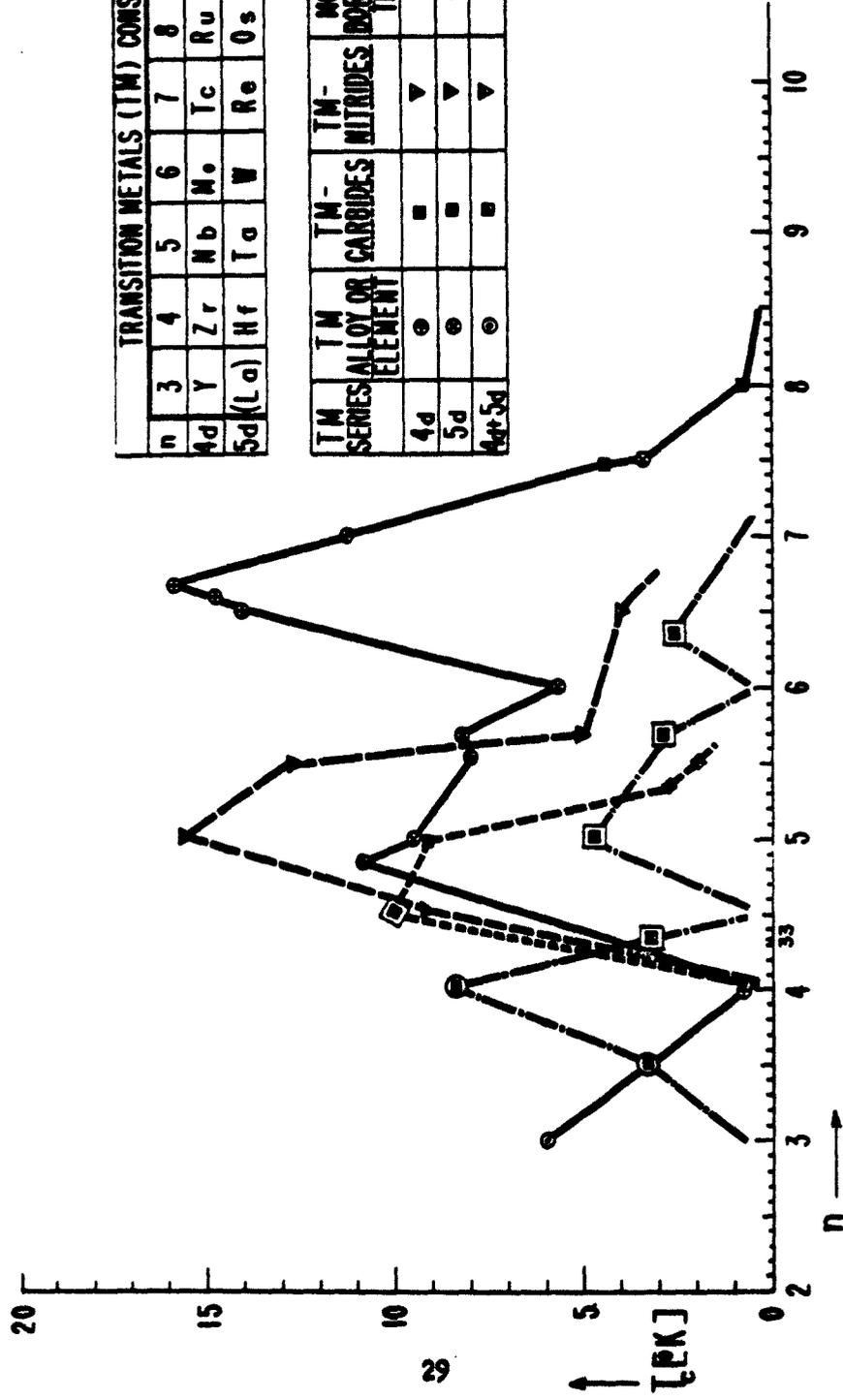
Figure 3

Maximum reported[6] transition temperatures, T_c, for the elements of the 4d and 5d transition metals (TM) and their alloys, and of the borides, carbides and nitrides formed with these metals as function of n, the average number of electrons per atom of the superconducting material. The boride curve is irregular, having a peak at n = 4.
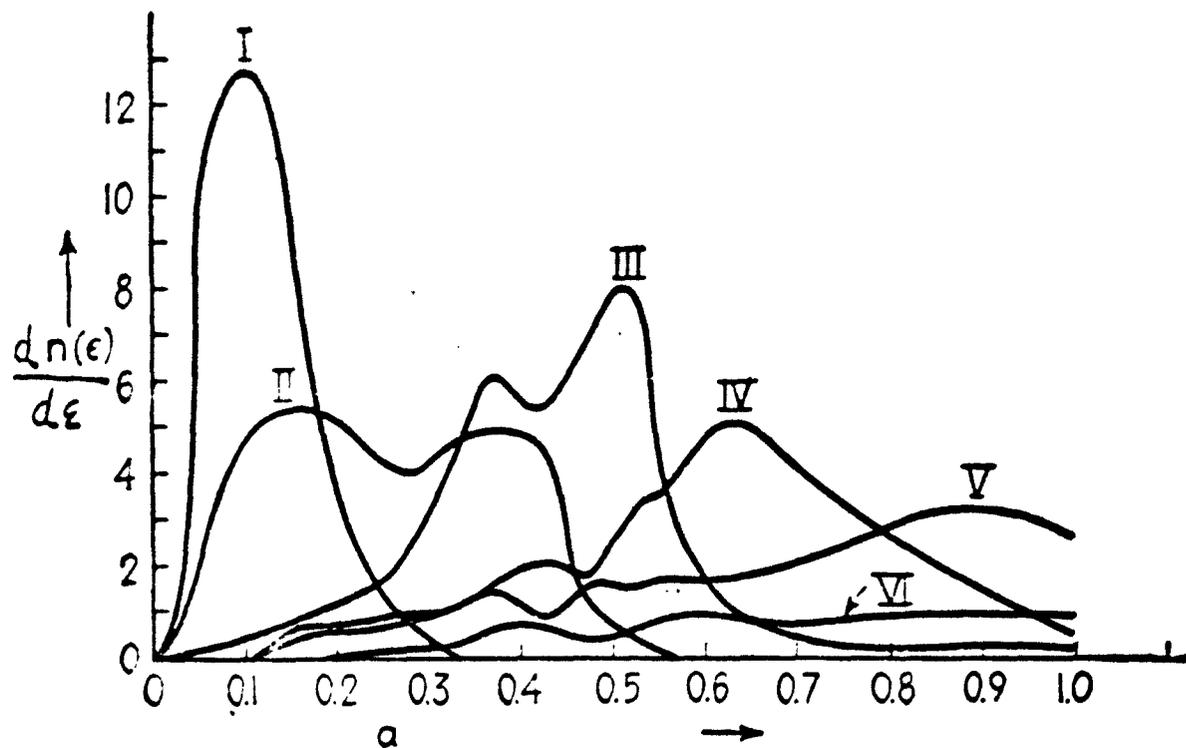
Figure 4
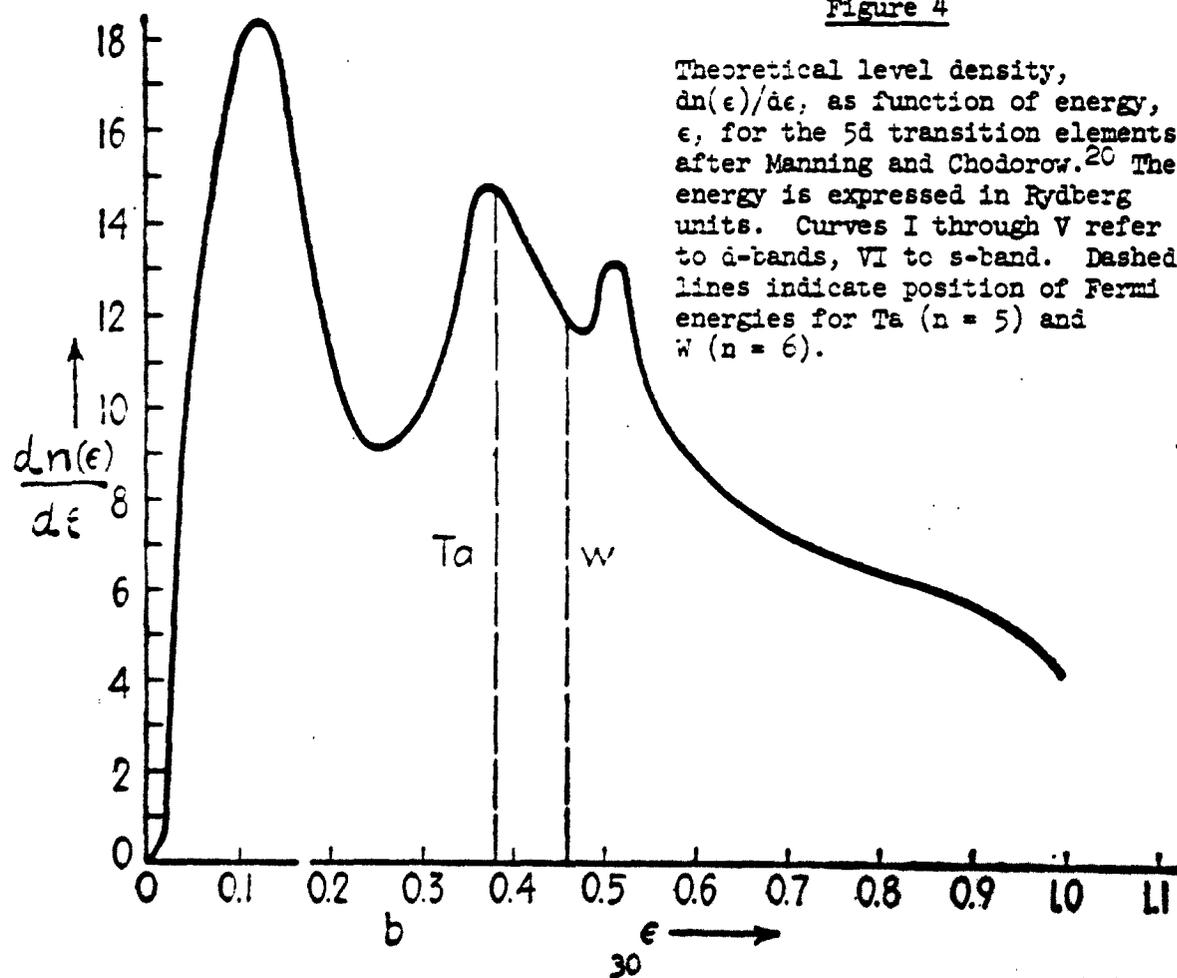
Theoretical level density, $dn(\epsilon)/d\epsilon$, as function of energy, ϵ, for the 5d transition elements, after Manning and Chodorow.[20] The energy is expressed in Rydberg units. Curves I through V refer to d-bands, VI to s-band. Dashed lines indicate position of Fermi energies for Ta ($n = 5$) and W ($n = 6$).
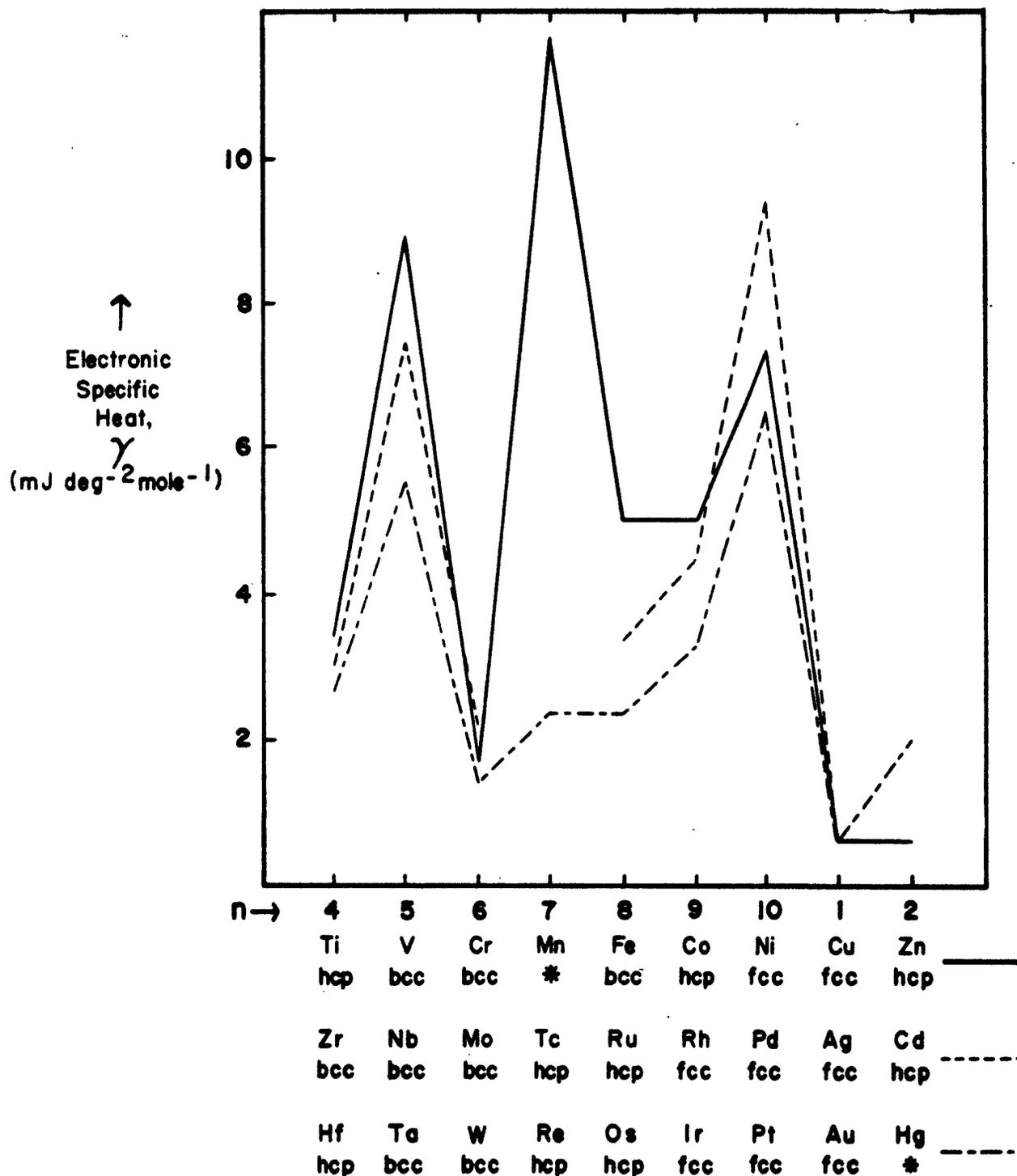
Figure 5

Electronic specific heats, γ, for the 3d, 4d, and 5d transition series, after Hoare.[23] Structure symbols as in Figure 1. Complex structures are indicated by *.

Figure 6

Representation of the T_c vs. n variation of the transition metal borides, analogous to Figure 3. The number of electrons per transition metal (TM) atom is indicated by n^*. Note peak for $n^* = 5$, valley for $n^* = 6$ for "E" material.

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β – MoB, (OOI) PLANE

BORON ATOMS
METAL ATOMS

■ ●   ● ●
○ X   ○ X
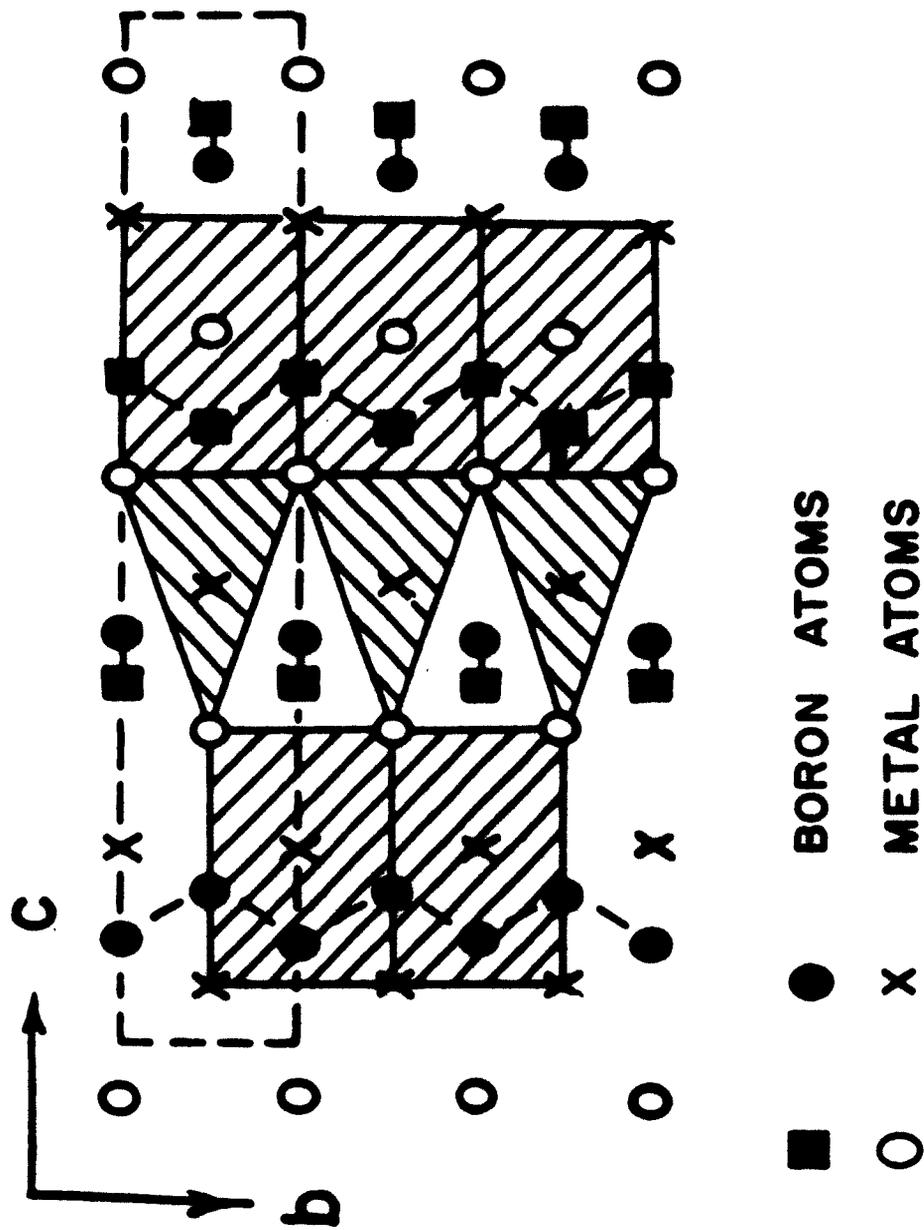
Figure 7

Structure of the monoborides β-MoB, MoB, FeB, and CrB, after Andersson and Kiessling.36
The structure of δ-MoB is similar.

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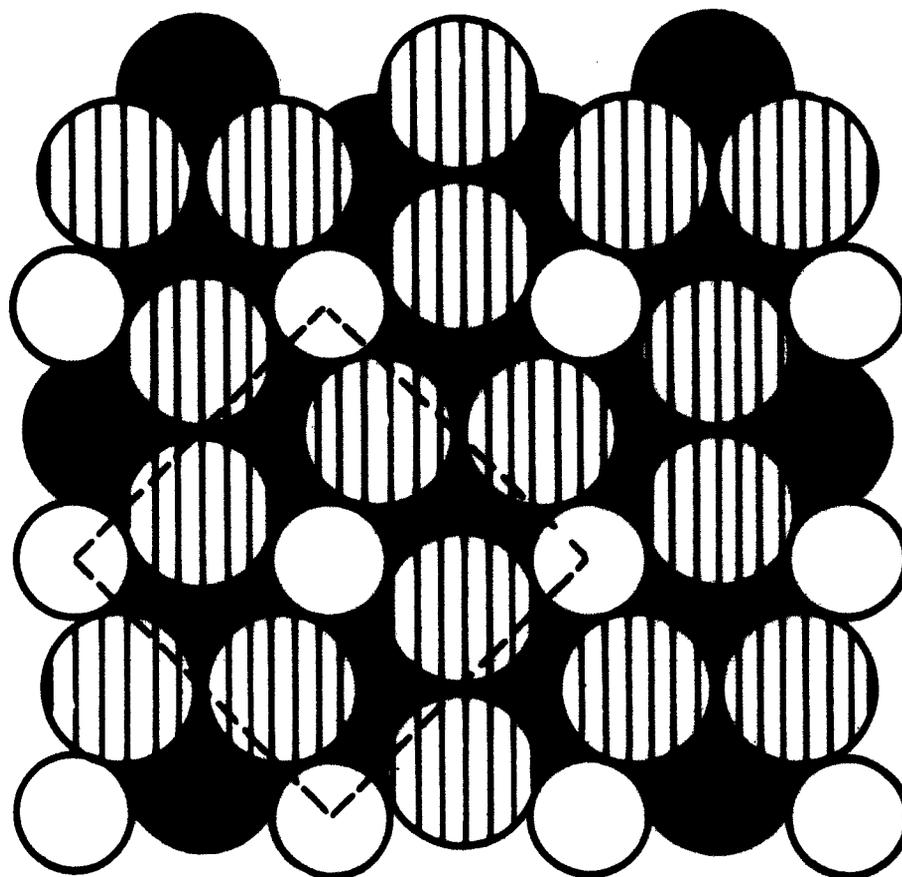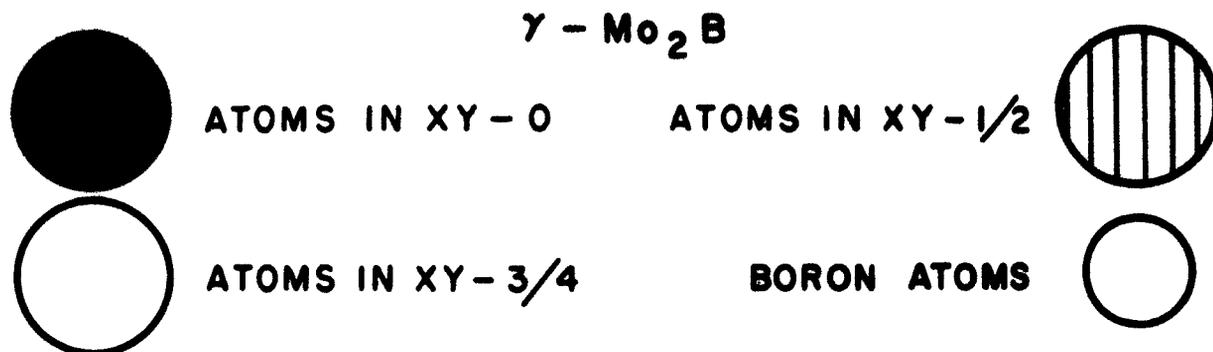
$\gamma - Mo_2 B$

Figure 8

Structure of the subborides γ-Mo$_2$B and Ta$_2$B, after Kiessling.[37] Large circles denote metal atoms, small circles boron atoms.
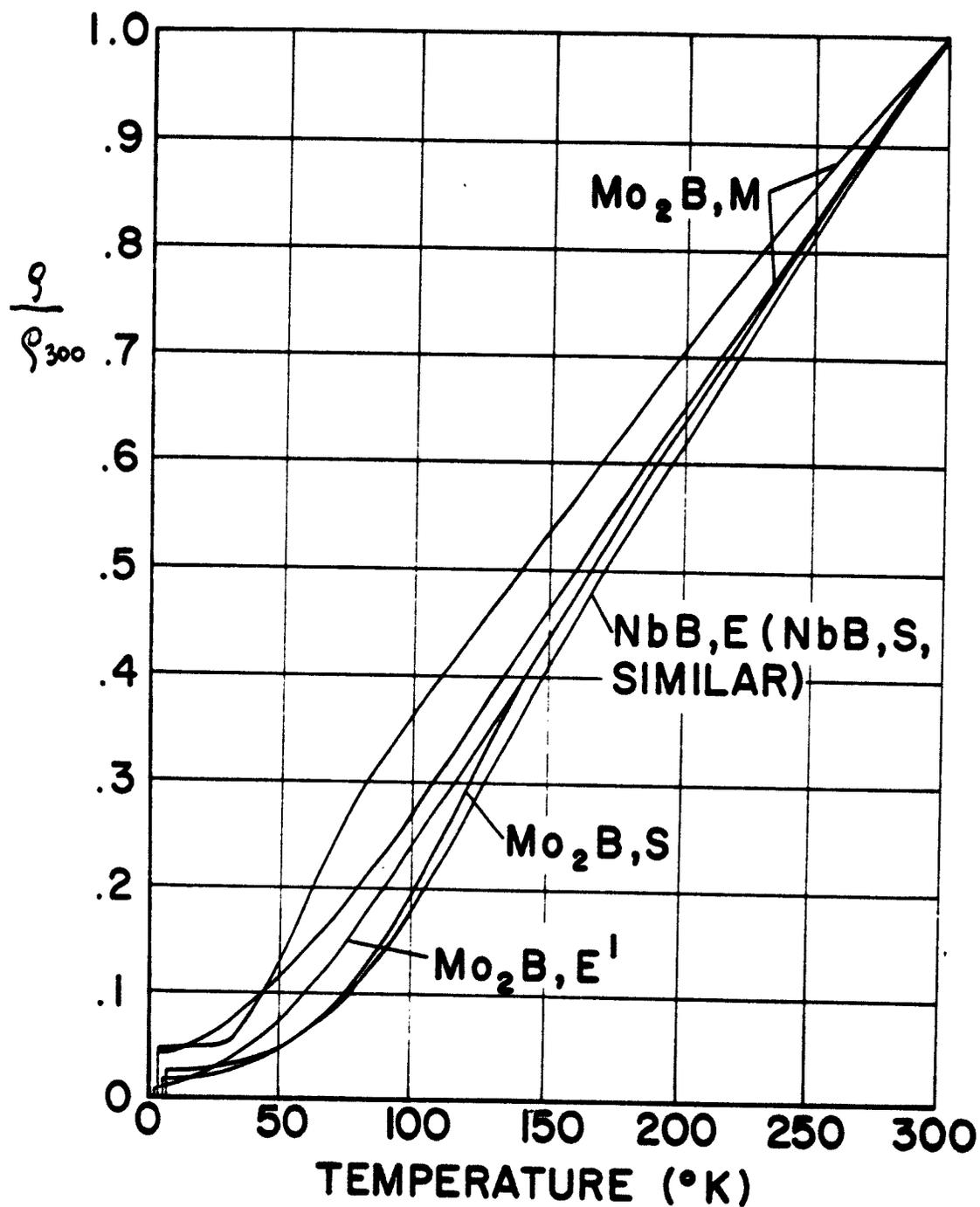
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Table I

Comparison of samples of NbB, MoB and "Mo$_2$B."

Explanation of Symbols:

S - Sintered in argon atmosphere at 1700°-1750° in copper crucible

M - Sintered rods molten in water-cooled copper crucible

M' - E Material molten in cold hearth in purified N$_2$ for 10 minutes at 2200°C

E - Electron beam melted and zone refined three times

E' - Electron beam melted and zone refined only one time

δ-MoB, γ-Mo$_2$B - Low temperature phases[36,37,38]

β-MoB - High temperature phase[36]

* - Sample resistance ($\mu \Omega$)

+ - (T$_n$) - Lowest temperature at which nonsuperconducting sample was measured

++ - ρ_{Tn}/ρ_{300}

For structure definitions see ASTM X-Ray Powder Data File.[38]

TABLE I

SAMPLE	ORIGINAL COMPOSITION	PREPARATION	IMPURITIES (≥10 PPM)												STRUCTURE	n	T_c (°K)	H_c (kOe at 4.2°K)	S_{300} ($\mu\Omega$-cm)	$\frac{S_r}{S_{300}}$
			Fe	Si	Al	Mn	Ti	Mg	Ta	Co	W	O₂	H₂	N₂						
20225 NbB₂	45 MOLE % Nb	S	100	<50	20	<20	<50	500			<300	500			Nb, NbB MINOR CONSTIT.	3.67?	6.40	8.00	8.120	.0345
			↖ (OTHER IMPURITIES: C-200, Zr<200, CuK40₂) ↙ (Ca, Cr, Na, Ni, Pb, Sn, V, Zn, <20)																	
20227 NbB	40.7 MOLE% Nb	S	100	<50	20	<20	<50	500			<300	500			Nb, NbB₂ MINOR CONSTIT.	4?	4.60	4.88	14.76	.0366
20516 NbB	50 MOLE % B	E	<100	<100			10	2000							β NbB TYPE STRU.	≥4	6.94	4.45	9.720	.0261
20517 NbB	3 MOLE % EXC.B	E	<100	<100			10	2000							β NbB " "	≥4	5.51	5.05	10.57	.0279
IIII3 NbB	49 MOLE % B	S	50	10	10	10	10								β NbB + δNbB, 3:1	4.5	<1.57⁺		92.35	.0576⁺
20507 NbB	50 MOLE % B	S	50	10	10	10	10								δ NbB	4.5	<1.65⁺		79.38	.3730⁺
IIII4 NbB	51 MOLE % B	S	50	10	10	10	10								β NbB + δ NbB, 3:1	4.5	<1.59⁺		68.54	.1308⁺⁺
20469B NbB		E	30	10			10								δ NbB γ Nb₂B, 3:2	4.5	<1.59⁺		37.62	.0126⁺⁺
10628 Nb₂B	6 MOLE % EXC.B	M														≥5	4.42		131.0	.0470
10629 Nb₂B	5½ MOLE % EXC.B	M														≥5	4.25		227.0	.0444
10630 Nb₂B	33 MOLE % B	S	40	20	10		10								γ Nb₂B + βNbB + Nb, 25:1:1	5	4.75		49.45	.0096
20508 Nb₁.₈₂B		S	200	500	10		10				600	232	135	254	γ Nb₂B + δNbB, 20:1	≤5	4.58	1.02	56.51	.0191
20469A Nb₂.₂B		E	20	<20	10		10								γ Nb₂B	≤5	<1.57⁺		70.35	.0284⁺⁺
20420 Nb₁.₉₈B		E'	20	300	10		10				20	600	49 4	36	γ Nb₂B	≤5	2.05		24.47	.0077
20469A-I Nb₂.₂B	20469A + N₂	M'	20	<20	10						800	102	10	26		≤5	4.35		25.33	.0036

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Table II. Survey of the discussed rules for the occurrence of superconductivity

Matthias Rule

for Elements:

(1a) Elements which are nonmetals, semiconductors or semimetals do not superconduct.

(1b) Elements which are antiferromagnetic do not superconduct.

(1c) Elements which are ferromagnetic do not superconduct.

(2) With n for the number of valence electrons, superconductivity is found only in elements for which $2 \leq n \leq 8$.

for Alloys, Compounds:

(1'a) Materials with the electronic properties of nonmetals, semiconductors, or semimetals do not superconduct.

(1'b) Antiferromagnetic materials do not become superconducting.

(1'c) Ferromagnetism resulting from d-spins, i.e., from unpaired electrons in partly filled d-subshells, is not compatible with superconductivity.

(1'd) Ferromagnetism resulting from f-spins is in special cases compatible with superconductivity

(2') With n now denoting the average number of valence electrons per atom of the alloy or compound, the occurrence of superconductivity is again limited by: $2 \leq n \leq 8$.

Table II (cont)

(3) The variation of T_c with n is given by an empirical function T(n). For a d-transition series, T(n) has relative maxima at n = 3, 5, and 7, and relative minima at n = 4, and n = 6. For a sequence of nontransition metals, T(n) increases monotonically with n.

(4) With V_a for the atomic volume, and M for the atomic mass, T_c varies for a given n as:

$$T_c \propto V_a^u / M^w; \text{ with } 4 < u < 5.$$

Observed T_c differences between isotopes of a number of elements suggest: $w \approx 1/2$, i.e., Elements at the limits given by (2), with n = 2 and n = 8, show no regular variation of T_c with V_a and M.

(5) The crystal structure has some influence on T_c. Uncomplicated cubic and hexagonal systems appear "favorable" to superconductivity. The variations in T_c which can be attributed to differences between structures are generally small (20% to 30%).

(3') The variation of T_c with n is again given by an empirical function T(n), which resembles that for the elements, but with the second maximum shifted to n ≈ 4.7 and the third maximum shifted to n ≈ 6.7.

(4') With V_a now denoting the mol-volume, the variation of T_c for a given n may be expressed by:

$$T_c \propto V_a^u \cdot F(M_1, M_2); \; 5 < u < 10.$$

No simple function $F(M_1, M_2)$ describing the combined influence of two atomic masses M_1, M_2 can be given although it is evident that large masses tend to decrease T_c.

(5') The uncomplicated cubic and hexagonal systems are again "favorable" to high T_c values. Several high T_c materials are intermetallic compounds of the type TM_3L (with "TM" for "transition metal," and "L" for another element) and crystallize in the β-W structure, which has no analogue among the elements. Numerous complicated structures among the medium and low temperature superconductors. No superconductors have structures without a center of inversion.

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Table II (cont)

Effects of Compound Formation

(A) The T_c values of all superconducting elements are substantially raised upon formation of suitable compounds or alloys. The increases are 50% and more for transition metals, and generally less for non-transition metals.

(B) With the exception of the elements of the f-transition series (rare earths and actinides) and of the 7a and 0 columns (halogens and inert gases) of the Periodic Table, most nonsuperconducting elements form superconducting alloys or compounds.

(C) Elements which become superconductors upon formation of an amorphous phase do so also upon formation of a suitable (generally not amorphous) compound. The same applies to elements which have a substantially raised T_c value in an amorphous phase.

(D) In certain compound systems containing transition metal atoms in the form of chains or the like, the T_c value is given by the chains alone and not by the averages over all the constituent atoms of the compound.

SUMMARY

The Matthias Rule for the elements is given by (1) through (5), see Section II. An analogous formulation for the alloys and compounds of the Matthias Rule is presented by (1') through (5'). Only compositions with at least 50 atom % of the element in question are considered. A, B, C, describe general effects of compound formation (see Section III). D pertains to compounds with transition metals arranged in chains or the like (see Sections V, VI).

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